AUTOXIDATION OF FATS AND ITS PREVENTION WITH ANTIOXIDANTS

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ABSTRACT

This paper present the mechanism of the reaction of fat degradation and its prevention with the help of antioxidants. Food degradation is a serious problem with which people confrunt bouth during the processing of the raw material and during food storage. In this way, we have presented the steps of the degradation, factors that influence and the way the antioxidant act

Keywords: antioxidant, unsaturated fatty acids, peroxides

INTRODUCTION

In general, the self-life of most food components, such as proteins, fats, carbohydrates, vitamins, is limited. Fats in particular are very susceptible to deterioration. The symptoms, off-taste and off-odour, are usually described as "rancidity" .

Strictly speaking, we have to distinguish between several types of fat deterioration, as each one occurs under specific conditions:

Hydrolysis : Fat molecules are split into glycerol and free fatty acids. The presence of humidity is necessary for this biochemical (due to microorganisms of enzymes) or chemical reaction.

*Polymerization:*Fat molecules exposed to high temperatures tend to form three-dimensional networks.

Autoxidation: Mainly unsaturated fatty acids oxidize in presence on oxygen.

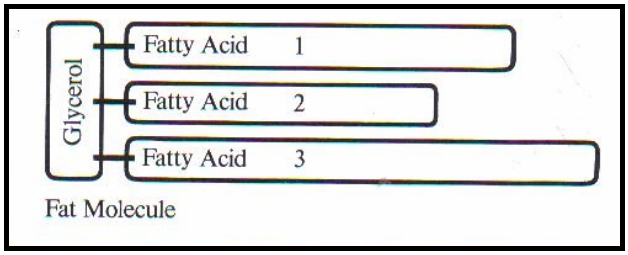
In foods, *autoxidation* is by far the most important type of fat deterioration. These leaflets will acquaint you with

- the autoxidation of fats
- the methods of retarding autoxidation.

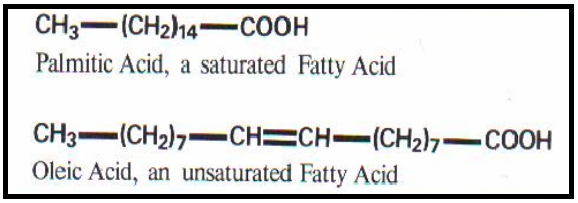
Detailed knowledge of the autoxidation reaction enables us to find possibilities for its successful retardation. Further – more, various methods for evaluating the susceptibility of fats to oxidation become accountable thanks to this knowledge.

A fat molecule consist of glycerol combined with three fatty acids.

The properties of a fat are determinated by the composition of its fatty acids.



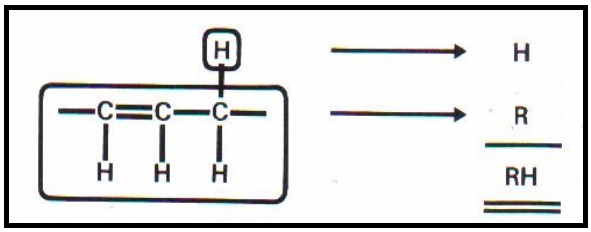
In contrast to saturated fatty acids, unsaturated fatty acids are highly susceptible to oxidation.



The hydrogen atom "H" in the neighbourhood of a double bond in an unsaturated fatty acid is extremly reactive.

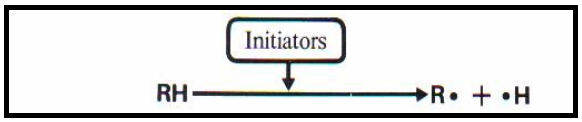
According to general custom , the fatty acid residue is designated as "R" .

Autoxidation starts in the vicinity of a double bond.



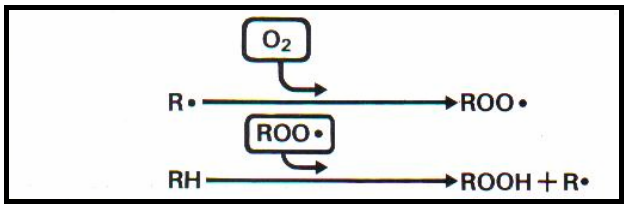
The autoxidation of unsaturated fatty acids can be devided into three phases: *initiation, propagation* and *termination.*

Initiation : Initiators, such as energy (light, heat) , traces of heavy metals, and peroxides attack the substrate RH and produce higly reactive free radicals ($R^{\bullet}$).



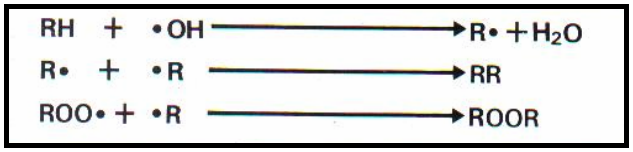
Propagation : Free radicals react with oxygen to produce peroxide radicals ($ROO^{\bullet}$).

Peroxide radicals have ability to attack another fatty acid RH : the result is a *peroxide (ROOH)* and a new free radical.

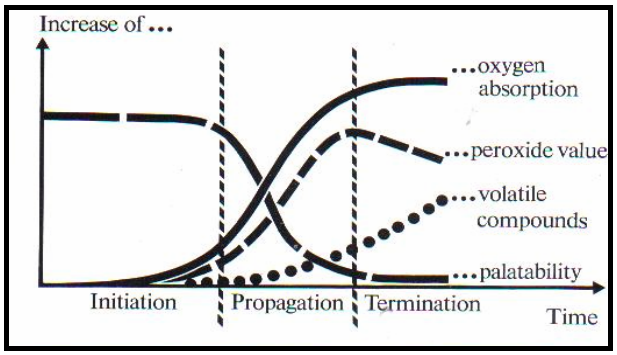


Peroxides are unstable compounds which are decomposed to radicals again, aldehydes, ketones, and alcohols. The volatile decomposition products are responsible for the *off-odour*.

*Termination:*The quantity of highly reactive compounds rises constantly until they begin to interact. Then the concentration of radicals and peroxides falls. Stable deterioration products are formed.



The three phases of fat deterioration are clearly distinguishable. The following diagram demonstrates the development of some parameters in the course of autoxidation. With their aid it is possible to judge the quality of a fat and to estimate its resistance to autoxidation.



A fat loses its palatability during the propagation phase. Therefore the duration of the initiation phase is a measure of its resistance to autoxidation.

Several methods are known for the determination of length of the initiation phase. The most reliable results are reached by storing the product in question under realistic condition and by subjecting it to organoleptic tests.

As a matter of convenience, such tests are usually "accelerated", e.g. by increasing the temperature of the system. These tests are based on the measurement of the increase of a certain compound produced in the course of the oxidation:

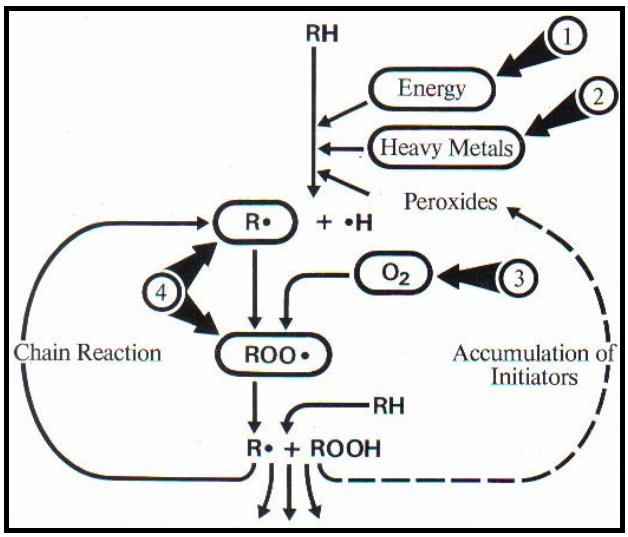
- Volatile acids: measuring of the induction time of the fat by Rancimat-test (the method most commonly used)
- Peroxides and hydroperoxides : determination of the peroxide value, diphenyl – carbazid method.
- Carbonyl compounds (ketones, aldehydes): heptanal value, benzidin value, anisidin value, thiobarbituric acid value, determination of volatile compounds (hexanal, hepatanal, etc.) by gas chromatography.

- Hydrocarbons : determination of pentane or other alkanes by headspace gas chromatography (advantage :extraction not necessary).

Autoxidation is an irreversible process of deterioration. It is not possible to prevent it completely, it only can be retarded.

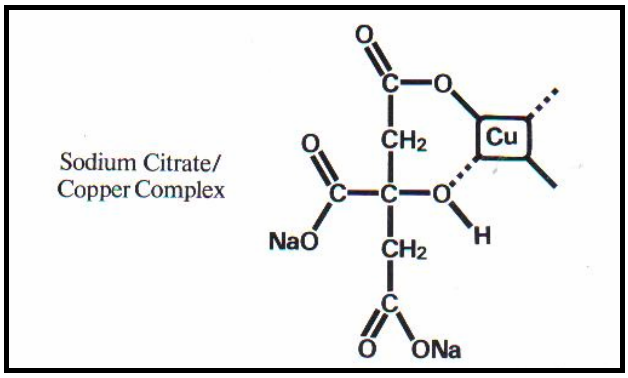
The following diagram summarizes briefly the initiation and the propagation phases and states the ways of retarding the undesired chemical reactions:

1. input of energy has to be at a minimum.
2. contact with traces of heavy metals have to be avoided
3. oxygen has to be substantially excluded
4. radicals have to be intercepted.



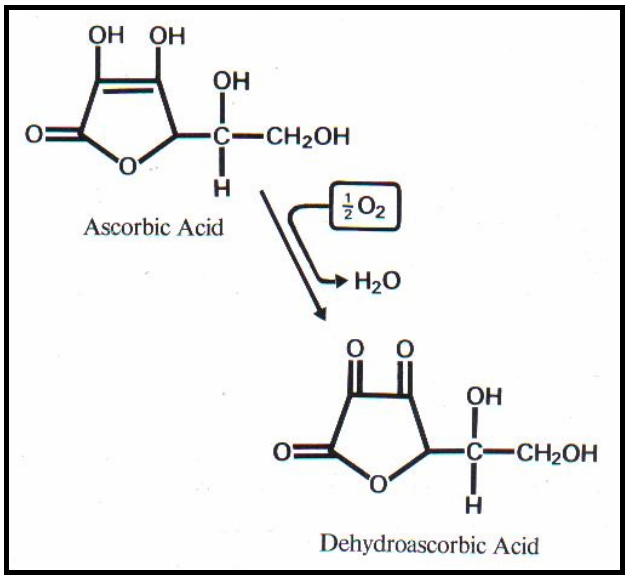
① The initiator *Energy* – light and heat – is best excluded by storage of fat in a cool , dark place. This is always the firsd preventive measure.

② *Heavy Metal Traces* are imported initiators. Even in concentration as low as 0,1 - 1 ppm, these catalysts may affect the stability of fats. Apparatus made from iron or copper are therefore not recommended. Traces of such metals can often be rendered harmless by combining them chemically with complexing agents such as citric or tartaric acids, their salts and esters, EDTA, lecithin, etc.



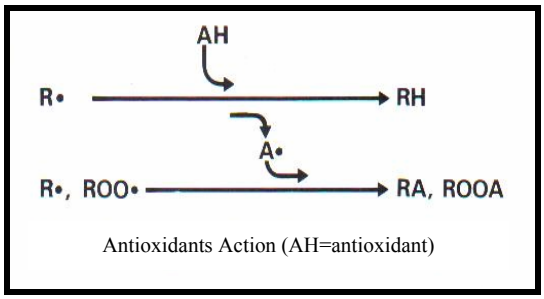
③ Contact of fats with *Oxygen* has to be avoided. Remaining or penetrating oxygen can be removed by oxygen scavengers which convert oxygen into a harmless form. Examples include ascorbic acid and its fatty acid esters such as ascorbyl palmitate and ascorbyl stearate.

④ *Radicals* can be inactivated by combining them with agents known as radical scavengers. Elimination of radicals interrupts the chain reaction.
In a first phase radical scavenger donate hydrogen atoms to free radicals. Additionally they can be combined directly with radicals to form inert products. Examples of radical scavengers include tocopherols, gallates, BHA,BHT.



Oxygen scavengers and radical scavengers are commonly called *antioxidants.*

Metal complexing agents and all substances sustaining the activity of antioxidants are designated *synergists.* Their contribution is essential for optimum retardation of autoxidation: In many cases , synergists substantially reduce the antioxidant requirement.



Antioxidants Action (AH=antioxidant)

MATERIALS AND METHODS

In the experimental determinations we have studied, the influence of antioxidants: ascorbyl palmitate and d-α- tocopherols (alone and in mixtures) on a sample of warmed lard at 65°C, going through the following stages:

1. The lard has been deposited in broad plates at a temperature of 65°C
2. The antioxidant has been dissolved in a small quantity of warmed lard at 100°C and then it was incorporated in the whole sample; in some of them we used lecithin.
3. We made 5 tests with different quantities of antioxidants and a control test, without antioxidants.
4. we determined periodically the peroxide index (using the tiosulphatemetria volumetric method) expressed in miliequivalent on kilograms of lard.
5. we established the time needed for each sample to reach the critical value of the peroxide index of 20 meq/kg .

RESULTS AND DISCUSSIONS

After the experiments we obtained the following results:

Sample	Antioxidants and synergists (mg/kg lard)			Duration (days)
	Ascorbyl palmitate	dl-Alpha tocopherol	Lecitin	
Control	0	0	0	1
1	250	0	0	4
2	0	50	0	4
3	0	0	700	1
4	250	50	0	17
5	250	50	700	30

- We could notice that the control sample and sample no 3 (with an addition of lecithin, without antioxidants) reach Ip= 20 meq/kg after 1 day (24 hours).
- Sample no 1 and 2 containing a single antioxidant reach Ip= 20 meq/kg after four days;
- Sample 4 containing two antioxidants reaches Ip=20 meq/kg after 17 days;
- Sample 5 containing the same quantity of antioxidants as sample 4 but also the amount of lecithin as sample no 3, reaches Ip= 20 meq/kg after 30 days;

CONCLUSIONS

The results obtained demonstrate that the mixture formed of palmitate ascorbyl , d-α-tocopherole and lecithin, determine the reaching of the critical peroxide index after 30 days of depositing at 65°C.

The mixture of antioxidants and lecithin has given the best results compared to the antioxidant alone; here it is manifested the synergetic action of the two antioxidants and the action of complexation of the lecithin manifested on some initiators of the rancidity reaction (for example traces of heavy metals)

Adding antioxidants and synergetic agents must be done both for into the raw material unprocessed and during the processing , ever since the initiation phase.

After a while when the chain reaction starts the antioxidants are absorbed to a great extent by the oxidation products already formed

reducing thus the minimal duration of validity of the food product.

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